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Abnormally narrow spectrum of localized states in amorphous silicon nitride

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The energy spectrum of localized hole states in amorphous silicon nitride (Si_3N_4) was determined using the method of thermally stimulated depolarization. The energy of the hole trap is 1.15 eV. The width of the spectrum of hole localized states does not exceed 10 meV, which is less than $kT = 26$ meV at room temperature. This result indicates that the broadening of the level of localized states, due to the absence of long-range order in amorphous Si_3N_4, i.e. due to fluctuations of the Si-N interatomic distance, N-Si-N tetrahedral angle and Si-N-Si dihedral angle, is small.

Keywords: thermally stimulated depolarization, silicon nitride, traps, multiphonon ionization mechanism.

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1. Introduction

The amorphous semiconductor and dielectics are characterized by absence of long-range order in location of atoms, and by presence of localized states (traps) [1,2]. Absence of the long-range order in amorphous semiconductors and dielectrics can cause potential fluctuations resulting in broadening of the discrete levels [1,3]. Typical dielectric with high ($10^{18}-10^{21}\,cm^{-3}$) concentration of traps and wide (4.5 eV) band gap is amorphous silicon nitride (Si_3N_4) [4,5]. Transfer and localization of electrons and holes in traps in Si_3N_4 are basis of operation principle of modern flash-memory of new generation [6], and memristors [7–10]. Currently the amorphous Si_3N_4 is model material to study processes of localization and transport of charge in dielectrics [11–21]. Si_3N_4 is tetrahedral compound, where Si atom is coordinated with four N atoms, and N atom is coordinated with three Si atoms [4]. In Si_3N_4 there are fluctuations of interatomic distance Si-N, tetrahedral angle N-Si-N and dihedral angle Si-N-Si [17,18]. It is identified that as trap responsible for localization of electrons and holes in Si_3N_4 the defect — Si-Si bond [12,13,15]. Fluctuations of interatomic distance, tetrahedral and dihedral angles can result in broadening of the energy spectrum of traps in Si_3N_4. Figure 1 shows spectra of localized states for electrons and holes in Si_3N_4 as per data of different papers [19–21]. Literature data on spectrum of electron and hole traps in Si_3N_4 can be qualitatively divided into three groups (Figure 1): 1) discrete spectrum (*a*) [19]; broadened Gaussian spectra (*b*) [20]; 3) continuous broad spectra (*c*) [21]. Method of thermostimulated depolarization (TSD) is an effective method of spectroscopy of localized states in semiconductors and dielectrics [22–24].

The present study task is determination of nature of spectrum of hole traps in Si_3N_4 by TSD method.

2. Experiment and calculation procedure

Structures Al-Si_3N_4 (40 nm)-SiO_2 (2 nm) — Si (of *p*-type, $\rho \approx 10\,\text{Ohm}\cdot\text{cm}$) were studied. The amorphous silicon nitride was obtained at 800°C by pyrolysis of mixture $SiCl_4+NH_3$. Ratio $SiCl_4/NH_3$ was 1/10. Si_3N_4 polarization by holes was performed at negative potential on Al. Value of trapped charge was monitored by voltage measurement

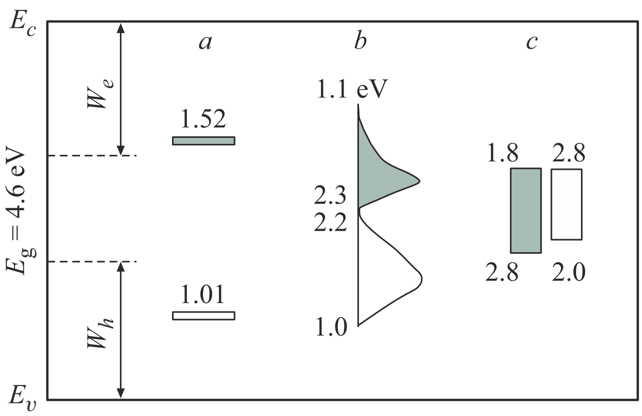

Figure 1. Energy spectrum of localized states for electrons and holes in amorphous Si_3N_4 as per data from different papers. Numbers inside the Figure mark values of trap energy taken from papers: *a* — [19], *b* — [20], *c* — [21].

of flat bands (U_{FB}), at the end of structure charging it was 3.1 V. Depolarization was performed at small positive potential (4 V) on Al at temperature linearly increasing with rate 1 K/s. The hole current of depolarization was registered during the structure heating from 300 K to 650 K.

For the theoretical description of charge transfer the one-band model is used (injection and transfer of electrons are neglected) . Heterogeneous electric field in Si_3N_4 is calculated using Poisson equation. In paper three models of the energy spectrum of traps are considered: *1* — discrete level of trap, *2* — continuous spectrum of traps with three different energy levels and same concentration, *3* — Gaussian distribution of traps. To describe the charge transfer in Si_3N_4 the following equations were used:

$$\frac{\partial p(x,t)}{\partial t} = \frac{1}{e}\frac{\partial j(x,t)}{\partial x} - \sum_i \sigma v p(x,t)\big(N_i - p_i^t(x,t)\big) + \sum_i p_i^t(x,t) P_i(x,t), \quad (1)$$

$$\frac{\partial p_i^t(x,t)}{\partial t} = \sigma v p(x,t)(N_i(x,t) - p_i^t(x,t)) - p_i^t(x,t) P_i(x,t) \quad (2)$$

$$\frac{\partial F(x,t)}{\partial x} = -\frac{\partial^2 U(x,t)}{\partial x^2} = e\,\frac{p(x,t) + \sum_i p_i^t(x,t)}{\varepsilon\varepsilon_0}, \quad (3)$$

where index $i = a, b, c$ depends on number of energy levels of traps, P_i — probability of trap ionization at specified values of electric field (F) and temperature (T), U — electric potential, σ — trap cross-section, N_i — concentration of traps, p and p_t — concentration of free and trapped holes, e — electron charge, $v = 10^7$ cm/s — speed of drift of holes [25], $\varepsilon = 7.0$ — low-frequency dielectric permittivity of Si_3N_4. Speed of holes drift is linked with current density by relationship $j = epv$.

To describe charge transfer the model of multiphonon ionization of traps [26]. Within framework of this model the probability trap ionization is described by expression:

$$P = \sum_{n=-\infty}^{+\infty} \exp\left[\frac{nW_{ph}}{2kT} - S\coth\frac{W_{ph}}{2kT}\right] I_n \times \left(\frac{S}{\sin h(W_{ph}/2kT)}\right) P_i^{tun}(W_t + nW_{ph}), \quad (4)$$

$$P_i^{tun}(W_{tun}) = \frac{eF}{2\sqrt{2m^* W_{tun}}} \exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF} W_{tun}^{3/2}\right),$$

$$S = \frac{W_{OPT} - W_T}{W_{ph}},$$

where W_T — thermal and W_{OPT} — optical energy of traps ionization, W_{tun} — energy of carriers tunneling, W_{ph} — energy of phonons, k — Boltzmann constant, I_n — Bessel function, m^* — effective tunneling mass. As boundary condition for equation (3) the value is used of external voltage pulse U, applied to Al-contact. During polarization the injection current of holes from Si-substrate is calculated based on Fowler-Nordheim mechanism.

3. Comparison of experiment with calculation

3.1. Trap with discrete energy level

Trap with discrete energy level W_T and concentration N_0 is considered Figure 2, *a*. Figure 2, *b* presents the dependence of depolarization current on temperature. The satisfactory agreement of experiment and theory is observed. The following parameters of hole traps are obtained based on best agreement of experiment and calculation: $W_T = 1.15$ eV, $W_{OPT} = 2.3$ eV, $W_{ph} = 0.06$ eV, $N_0 = 4 \cdot 10^{18}$ cm^{-3}, $\sigma = 5 \cdot 10^{-14}$ cm^2, $m^*/m_e = 0.5$, m_e — mass of free electron. The obtained energy of trap $W_T = 1.15$ eV is close to trap energy 1.01 ± 0.03 eV, determined in paper [19].

3.2. Continuous spectrum of traps with three different energies and same concentration

Figure 3, *a* presents model of continuous spectrum of traps with three different energy levels W_T^a, $W_T^b = W_T$ and W_T^c, with $W_T^b - W_T^a = W_T^c - W_T^b$, where $W_T^b = 1.15$ eV, and same concentration $N_1 = N_2 = N_3 = N_0 = 4 \cdot 10^{18}$ cm^{-3}; *b* — TSD Si_3N_4 (experiment — squares) and calculation (solid line) for three different values of ΔW: 0.01, 0.1, 0.5 eV.

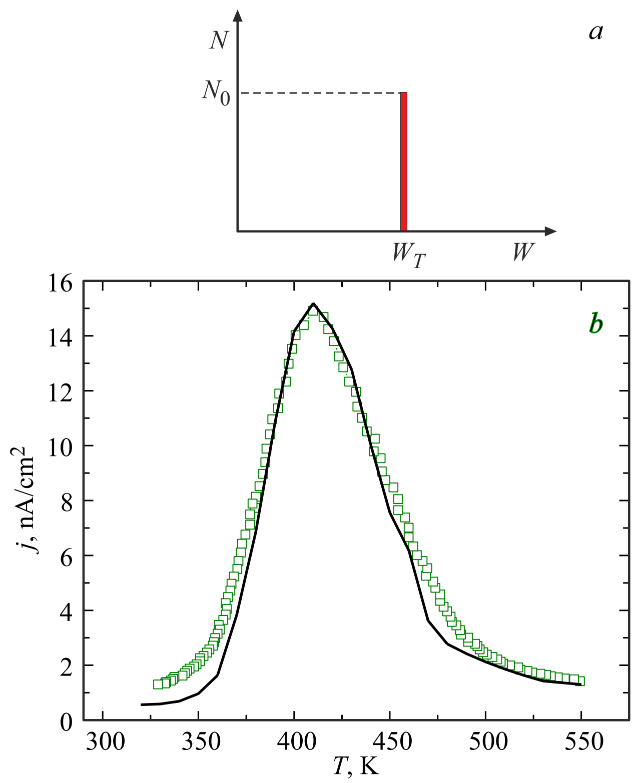

Figure 2. *a* — Model of discrete level of trap with energy W_T and concentration N_0 in Si_3N_4, *b* — dependence of current on temperature at positive voltage 4 V on Al. Squares — experiment, dashed line — calculation for discrete level with energy $W_T = 1.15$ eV.

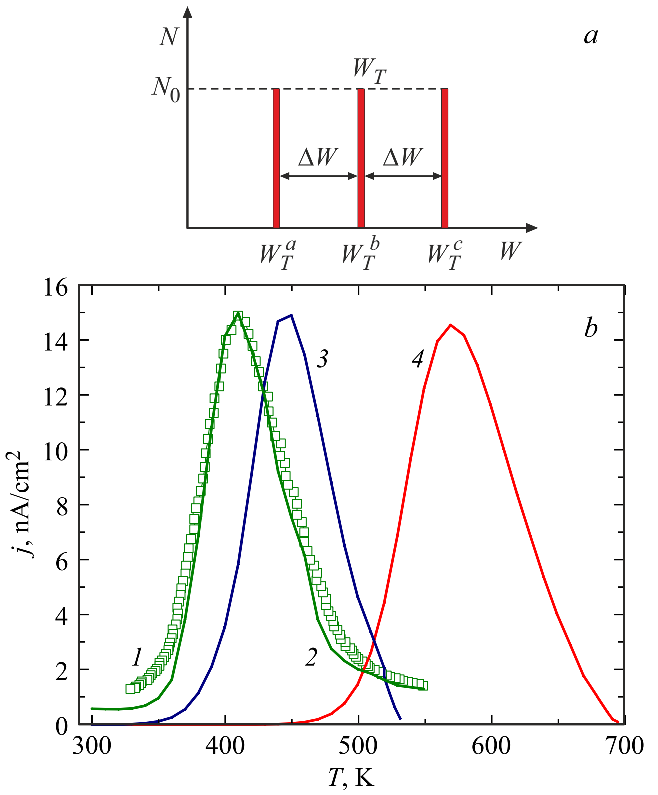

Figure 3. *a* — model of continuous spectrum of traps with three different energy levels and same concentration N_0; *b* — comparison of TSD experiment (*1* — squares) with calculation (*2, 3, 4* — solid lines) for model of continuous spectrum of traps with $W_T^b = 1.15\,\text{eV}$ at depolarization voltage 4 V. Values of dispersion (distance between levels of traps ΔW) is: *2* — 0.01, *3* — 0.1, *4* — 0.5 eV.

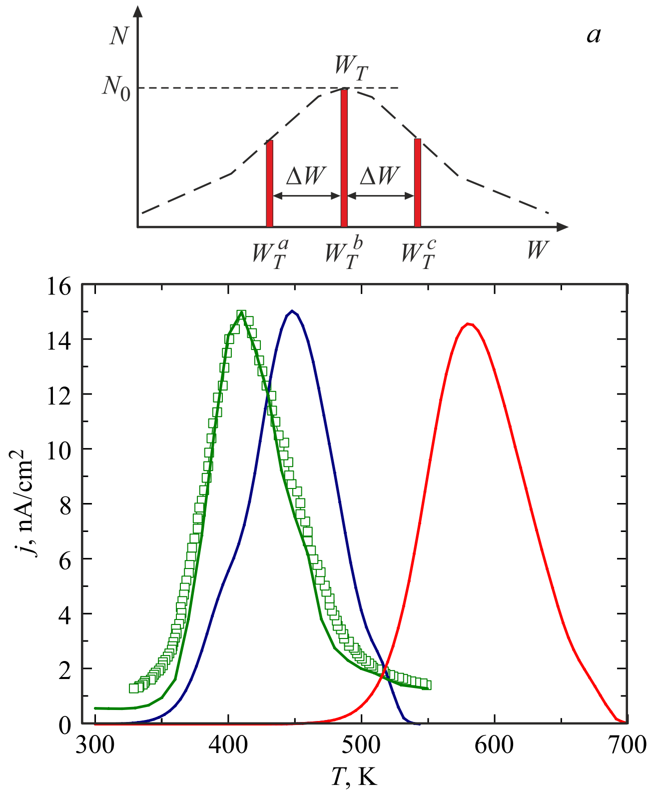

Figure 4. *a* — model when trap concentration is distributed as per Gaussian law depending on their energy, *b* — comparison of TSD experiment (*1* — squares) with calculation (*2, 3, 4* — solid lines) for Gaussian distribution of traps $c = 1.15\,\text{eV}$ at depolarization voltage 4 V. Values of dispersion (distance between levels of traps ΔW) is: *2* — 0.01, *3* — 0.1, *4* — 0.5 eV.

Figure 3 shows that increase in number of energy levels for traps does not result in better agreement with the experiment. For different ΔW values the calculation forecasts the presence of one peak in TSD spectrum corresponding to the deepest trap. For example, for $\Delta W = 0.5\,\text{eV}$, the deepest level will correspond to energy $W_T^c = 1.15 + 0.5 = 1.65\,\text{eV}$. ΔW increasing results in offset of the single peak of TSD towards higher temperatures (Figure 3, *b*). Traps with small energy make insignificant contribution into TSD spectrum (Figure 3, *b*). Height of TSD peaks in all cases is same due to same amount value of accumulated charge ($U_{FB} = 3.1\,\text{V}$), trapped in traps during structure polarization.

3.3. Gaussian distribution of traps

Figure 4, *a* presents model of spectrum of traps with three different energy levels (where $i = a, b, c$) and concentration N_i, distributed as per Gaussian law:

$$N_i = N_0 \exp\left(\frac{(W_T^i - W_T)^2}{2\Delta W^2}\right), \qquad (5)$$

where N_0 and N_i — maximum and calculated concentration of traps, respectively. For ΔW values 0.01, 0.1, 0.5 eV were used. Figure 4, *b* shows comparison of TSD experiment (squares) with calculation (solid lines) at traps concentration calculated as per formula (5) at $N_0 = 4 \cdot 10^{18}\,\text{cm}^{-3}$, at different values of ΔW. Figure 4, *b* shows that with ΔW increasing the offset of TSD dependences towards the higher temperatures is observed. Main contribution into TSD spectrum is made by deep traps with energy $W_T^c = 1.65\,\text{eV}$, though concentration of traps with energy 1.15 eV exceed the concentration of traps with energy $W_T^c = 1.65\,\text{eV}$.

Absence of contribution of traps with energy 1.15 eV into TSD spectrum is due to that in the mode of Si_3N_4 polarization the filling with holes is low as compared to filling of traps with energy 1.65 eV.

4. Discussion of results

TSD experiments are satisfactory described by the theory of multiphonon ionization under assumption that in Si_3N_4 there are traps with discrete level $W_T = 1.15\,\text{eV}$ (Figure 2, *b*). TSD calculation for case of continuous and

Gaussian spectrum of traps does not result in better agreement between the experiment and calculation (Figures 3, *b* and 4, *b*). In all cases upon the traps presence with different energies in Si_3N_4 in TSD spectra one peak was observed, which corresponds to deepest traps. Insignificant contribution of small traps into TSD spectrum is due to that under the mode of Si_3N_4 polarization, their filling is low as compared to filling of deeper trap. Scattering in literature of ideas relating spectrum of traps in Si_3N_4 (Figure 1) can be due to two causes: 1) different technology of Si_3N_4 synthesis; 2) different models used to describe the traps ionization.

5. Conclusion

In this paper TSD in Si_3N_4 was studied experimentally and theoretically. Experiment is satisfactory described by the theory of multiphonon ionization of holes traps with discrete level 1.15 eV. Broadening of the discrete level of trap in Si_3N_4, does not exceed 0.01 eV. TSD calculation for case of continuous and Gaussian spectrum of traps does not result in better agreement between the experiment and calculation. To model processes of write/erase and storage of charge, in flash-memory devices, based on the effect of localization of electrons and holes in Si_3N_4, the use of model of discrete spectrum of traps is justified.

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Conflict of interest

The authors declare that they have no conflict of interest.

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